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Physicochemical properties of the complex oxides in Sm-Ba-Me-Cu-O (Me = Fe, Co) systems

The present work was focused on the studies of crystal structure, oxygen non-stoichiometry, thermal expansion of $SmBaCo_{2-x}Cu_xO_{6-\delta}$ and $SmBaFe_{2-x}Cu_xO_{6-\delta}$. Values of the oxygen content in complex oxides $SmBaCo_{2-x}Cu_xO_{6-\delta}$ were determined over a wide temperature range in air using high temperature thermogravimetry and iodometric titration. Also, chemical stability with respect to $Ce_{0.8}Sm_{0.2}O_{1.9}$ and $Zr_{0.85}Y_{0.15}O_{1.93}$ two common solid electrolyte materials used for SOFCs was evaluated.

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Introduction

Layered perovskites compounds $AA'B_2O_{6-\delta}$ wherein A is a lanthanide partially substituted by alkaline earth metal A', and B is 3d-atoms of metal (Ti, Cr, Mn, Fe, Co, Ni, Cu), are currently under scrutiny due to the successful combination of their physico-chemical properties [1,3].

Physico-chemical properties of the oxides formed in systems $LnBaMe_{2-x}M_xO_{6-\delta}$, are directly dependent on their crystal structure, the formation that can be significantly affected by an oxygen content. In this regard, information on the method of production, physico-chemical properties and stability of oxides $AA'B_2O_{5+\delta}$ under variation of the chemical composition and external thermodynamic conditions today is up-to-date. Therefore, the aim of this paper is to receive, and to analyze the crystallical structure and physico-chemical properties of complex oxide phases forming in the systems $SmBaMe_{2-x}Cu_xO_{6-\delta}$ (Me = Fe, Co).

The experimental part

Synthesis of the samples for the study was carried out on glycerol-nitrate technology. To prepare the samples samarium oxide Sm_2O_3 and barium carbonate $BaCO_3$ were used as starting components; they were previously calcined to remove adsorbed moisture and gases, metallic cobalt, and iron oxalate $FeC_2O_4 \times 2H_2O$,

as well as nitric acid HNO_3 (qualification analytically pure), and glycerol (analytical grade qualification). Cobalt metal was prepared by reduction of corresponding oxides at 500–600°C in a stream of hydrogen. Thermogravimetric studies were carried out on the thermobalance STA 409 PC by Netzsch Gmbh., allowing to fixate changes in mass of the sample in dependence of the partial pressure of oxygen and temperature.

Measurements were carried out in static and dynamic modes. In the static mode, the sample (1–2 g), previously weighed in a platinum crucible, was heated to the temperature of the beginning of the measurements, it was held at this temperature for 10 hours to establish equilibrium between the solid and gas phases, and then the temperature was raised again and the constant of the weight of the sample was expected. Investigated temperature range of 300–1100 °C was held in the heating and cooling mode to 100 °C. In the dynamic mode the change in weight was continuously recorded during heating and cooling with a speed of 2 °C per min from room temperature to 1100 °C. The absolute value of oxygen deficiency was determined by direct reduction samples in hydrogen and iodometric titration methods. For this, the samples were slowly cooled to room temperature. Measurement of the linear coefficient of thermal expansion (LKTR) of ceramic materials is necessary to determine the possibility of obtaining of lasting contact in high-temperature electrochemical devices (such components are electrolytes, electrodes, electrical circuits, sealants, etc.).

Measurements of relative expansion of ceramic bars with increasing temperature were performed on dilatometer DIL402 C by Netzsch Gmbh in the temperature range 25–1100 °C with the heating and cooling rate of 5° per minute.

Results and Discussion

Complex oxides $SmBaCo_{2-x}SuxO_{6-\delta}$:

On glycerol-nitrate technology hard solutions were synthesized compositions $SmBaCo_{2-x}SuxO_{6-\delta}$ where $0 \le x \le 2$. XRD revealed that single-phase complex oxides $SmBaCo_{2-x}Su_xO_{6-\delta}$ form in the composition range $0 \le h \le 1.2$.

With minimal substitution of cobalt with copper ($x = 0.1$) a composite oxide is formed, which X-ray is satisfactorily described within the orthorhombic cell (pr. G. *Pmmm*).

Radiographs of the samples with a high content of copper ($0.2 \le h \le 1.2$) have been indexed within the tetragonal unit cell of the space group *P4*/*mmm*. In fig. 1 as an example of a complex oxide radiograph $SmBaCo_{1.4}Su_{0.6}O_{5+\delta}$ is represented. For all single-phase oxides unit cell parameters of the atomic coordinates were calculated. When the concentration of copper ions is increasing, an increase in parameters and volume of the unit cells of complex oxides $SmBaCo_{2-x}Cu_xO_{6-\delta}$ is observed. Such dependence can be explained in terms of size effects. Substitution of cobalt ions ($r_{Co^{3+}} / r_{Co^{4+}}$ = 0.75 / 0.67 Å, cn 6) with large size copper ions ($r_{Cu^{2+}} / r_{Cu^{3+}}$ = 0.87 / 0.68 Å, cn 6) [4] leads to a gradual increase in the bond lengths in the B-O, and as a consequence, increase in the size of the cell unit.

The phase composition of the samples $SmBaCo_{2-x}Cu_xO_{6-\delta}$, outside the homogeneity region is presented in Table 1.

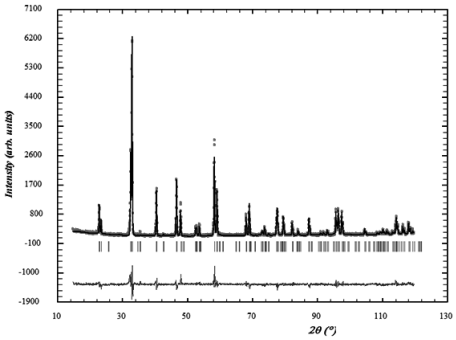

Fig. 1 XRD pattern $SmBaCo_{1.4}Cu_{0.6}O_{6-\delta}$, treated by the method of Rietveld. Points are experimental data; solid top shedding is theoretical spectrum; solid bottom line is the difference between the experimental data and the theoretical curve.

Table 1

Nominal composition of the samples	Phase composition of the samples
$SmBaCo_{0.7}Cu_{1.3}O_{6-\delta}$	$SmBaCo_{0.8}Cu_{1.2}O_{6-\delta}$
$SmBaCo_{0.6}Cu_{1.4}O_{6-\delta}$	$Sm_3Ba_3(Cu,Co)_6O_{14-2\delta}$
$SmBaCo_{0.4}Cu_{1.6}O_{6-\delta}$	$Sm_3Ba_3(Cu,Co)_6O_{14-2\delta}$
$SmBaCo_{0.2}Cu_{1.8}O_{6-\delta}$	
$SmBaCu_2O_{6-\delta}$	$Sm_3Ba_3Cu_6O_{14-2\delta}$

The compounds of nominal composition $Sm_3Ba_3(Cu,Co)_6O_{14-2\delta}$ are solid solutions $SmBa_{2-x}Sm_x(Cu,Co)_3O_{7-\delta}$ [4–6]. The crystal structure of these compounds has been described in terms of the tetragonal unit cell with triple option with ($a_p \times a_p \times 3a_p$) space group *P4/mmm*.

Figure 2 shows the temperature dependence of the oxygen content of complex oxides $SmBaCo_{2-x}Cu_xO_{6-\delta}$.

With the introduction of copper in cobalt sublattice a decrease in the value of the oxygen content is observed. This is due to the fact that the copper becomes totally or partially the electron acceptor (Cu'_{Co}) (EO_{Cu}=1.75) and contributes to the oxygen vacancy ($V_O^{\cdot\cdot}$) and/or electron holes.

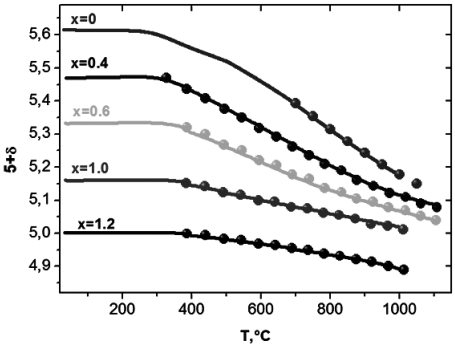

Fig. 2. The dependence of the oxygen content of the temperature for $SmBaCo_{2-x}Cu_xO_{6-\delta}$

Measuring of the relative increase in the size of the samples $SmBaCo_{2-x}Cu_xO_{6-\delta}$ (x = 0; 0.4; 0.6) was performed in air in the temperature range of 25–1100 °C at a rate of heating and cooling 2° per minute.

For this, the powders of the oxides were compressed under a pressure of 60 to 80 bar in the form of bars of size 2×4×20 mm via a hydraulic press. The resulting bars were sintered in air at 1050–1200°C for 14 hours and then slowly cooled to room temperature at a rate 100° per hour.

The density of the sintered layered perovskites of samarium-barium $SmBaCo_{2-x}Cu_xO_{6-\delta}$ is at least 90% of the calculated from the X-ray data.

Monotonic character of dilatometric dependencies for complex oxides $SmBaCo_{2-x}Cu_xO_{6-\delta}$ indicates the absence of phase transitions. It has been established that the value of the CTE decreases with increasing concentration of copper in $SmBaCo_{2-}xCu_xO_{6-\delta}$.

Chemical compatibility of complex oxides $SmBaCo_{2-x}Su_xO_{6-\delta}$ (x = 0; 0.2; 0.4; 1.0) with respect to the material of the electrolyte $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Zr_{0.85}Y_{0.15}O_{2-\delta}$ were studied by contact annealing at 900°C, 1000°C, 1050°C, and 1100°C in air.

XRD revealed that complex oxides $SmBaCo_{2-x}Su_xO_{5+\delta}$cx=0–0.4 do not react with a stabilized ceria oxide. And by annealing of the sample $SmBaCoSuO_{6-\delta}$ with $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ at a temperature of 1000 °C, the diffraction patterns of the annealed mixtures present reflexes related to the cobaltites and cuprates samarium and barium.

The electrolyte based on zirconia at a temperature of 900 °C is reacted with all samples of $SmBaCoSuO_{5+\delta}$. As the main impurity phase in the diffraction patterns of the annealed mixtures present reflexes related to $BaZrO_{3-\delta}$.

Complex oxides $SmBaFe_{2-x}Su_xO_{6-\delta}$:

Solid solutions $SmBaFe_{2-x}Su_xO_{6-\delta}$, where $0.5\leq x\leq 1.5$ with 0.1 step were synthesized by the glycerol-nitrate technology. According to X-ray data, solid solutions $SmBaFe_{2-x}Su_xO_{6-\delta}$ with $0.7\leq x\leq 1.3$ are single-phase. Radiographs of oxides $SmBaFe_{2-x}Su_xO_{6-\delta}$ are satisfactorily described in terms of the tetragonal unit cell of the space group *P4*/*mmm*. Example radiographs of solid solution $SmBaFe_{1.2}Su_{0.8}O_{6-\delta}$, treated by the method of full-profile Rietveld analysis are shown in Fig. 3.

For all single-phase oxides there were calculated unit cell parameters of the atomic coordinates. It was found that an increase in the concentration of copper in $SmBaFe_{2-x}Su_xO_{6-\delta}$ leads to a gradual increase in the parameters and the unit cell volume, which can be explained in terms of the size factor.

Conclusions

According to the results of the work, the following conclusions can be drawn:

1. The regions of homogeneous solid solution $SmBaFe_{2-x}Su_xO_{6-\delta}$ ($0.7\leq x\leq 1.3$), $SmBaCo_{2-x}Cu_xO_{6-\delta}$ ($0\leq x\leq 1.2$) in the air are determined. The dependences of the unit cell parameters of the composition are drawn. It is shown that an increase in the degree of substitution of cobalt and iron in copper is a monotonic increase in the parameters and scope of the unit cells in oxides $SmBaMe_{2-x}Cu_xO_{6-\delta}$;

2. It was found that the solid solutions $SmBaCo_{2-x}Cu_xO_{6-\delta}$ in the range of compositions $0.1\leq x\leq 0$ crystallize in the orthorhombic cell (pr. G. Pmmm), and complex oxides $SmBaFe_{2-x}Su_xO_{6-\delta}$ ($0.7\leq x\leq 1.3$) and $SmBaCo_{2-x}Cu_xO_{6-\delta}$ ($0.2\leq x\leq 1.2$) in the tetragonal (sp. gr. *P4*/*mmm*);

3. High thermogravimetry and iodometric titration methods determined the values of oxygen content in the complex oxides formed in systems Sm-Ba-Co-Cu-O in a wide temperature range in air. It was found that the introduction of copper reduces the oxygen content in $SmBaCo_{2-x}Me_xO_{6-\delta}$;

4. Coefficients of thermal expansion (CTE) of solid solutions $SmBaCo_{2-x}Cu_xO_{6-\delta}$ (x=0; 0.4; 0.6) are calculated. It

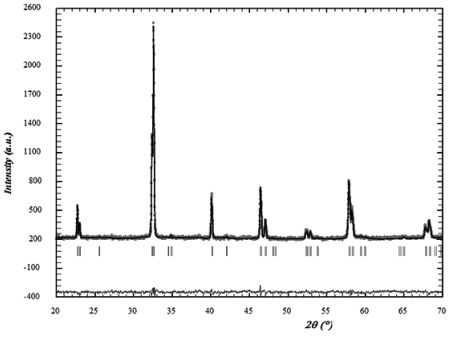

Fig. 3 X-ray data for $SmBaFe_{1.2}Su_{0.8}O_{6-\delta}$, treated by the method of Rietveld

is shown that the magnitude of the CTE decreases with increasing concentration of copper in the samples;

5. The chemical compatibility of complex oxides with the material of the solid electrolyte ($Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Zr_{0.85}Y_{0.15}O_{2-\delta}$) is researched at $900 \leq T$, $°C \leq 1100$ and Po_2=0.21 atm. It has been shown that solid solutions $SmBaCo_{2-x}Me_xO_{6-\delta}$ interact with stabilized zirconia at a temperature of 900 °C and do not interact with the stabilized cerium oxide to a temperature not higher than 900–1100°C depending on the concentration of copper ions.

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